

# ***Final Technical Report***

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## **Nanolaminates with Novel Properties Fabricated Using Atomic Layer Deposition Techniques**

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<b>14. ABSTRACT</b> This AFOSR grant worked on the development, understanding and applications of atomic layer deposition (ALD) for nanolaminates. ALD can be used to fabricate unique nanolaminates with novel properties. Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties that are not simply a "rule of mixtures". These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. The optimized nanolaminates may have important applications as better protective thermal barrier coatings and enhanced superlattice Bragg reflectors in the x-ray region. During the course of this research, the growth and characterization of W/Al <sub>2</sub> O <sub>3</sub> nanolaminates was examined as a model system. The W/Al <sub>2</sub> O <sub>3</sub> nanolaminate has revealed many fascinating thermal and optical properties. Very low thermal conductivity W/Al <sub>2</sub> O <sub>3</sub> nanolaminates were demonstrated that displayed thermal conductivities less than yttria-stabilized ZrO <sub>2</sub> . Extremely high x-ray reflectivities were also observed for W/Al <sub>2</sub> O <sub>3</sub> nanolaminates. In particular, world record x-ray reflectivities were observed in the hard x-ray region. The quality of the W/Al <sub>2</sub> O <sub>3</sub> nanolaminate is dependent on the nucleation and growth of the W and Al <sub>2</sub> O <sub>3</sub> nanolayers. Consequently, detailed experimental measurements and theoretical simulations have explored W ALD surface chemistry and the nucleation of W ALD on Al <sub>2</sub> O <sub>3</sub> . The project has aimed to establish correlations between thermal and optical properties and nanolaminate structure, interfacial density and composition.					
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## I. Overview

This AFOSR grant has worked on the development, understanding and applications of atomic layer deposition (ALD) for nanolaminates. Atomic layer deposition can be used to fabricate unique nanolaminates with novel properties. Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties that are not simply a "rule of mixtures". These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. Atomic layer deposition offers exquisite control for this optimization. The optimized nanolaminates may have important applications as better protective thermal barrier coatings and enhanced superlattice Bragg reflectors in the x-ray region.

We have studied the growth and characterization of W/Al<sub>2</sub>O<sub>3</sub> nanolaminates as a model system. The quality of the W/Al<sub>2</sub>O<sub>3</sub> nanolaminate is dependent on the nucleation and growth of the W and Al<sub>2</sub>O<sub>3</sub> nanolayers. Consequently, we have explored the surface chemistry of W ALD and have performed detailed experimental measurements and theoretical simulations of W ALD nucleation on Al<sub>2</sub>O<sub>3</sub>. Our objective has been a thorough understanding of the nanolaminate ALD growth to be able to fabricate precise nanostructures that display desired properties.

The precisely fabricated W/Al<sub>2</sub>O<sub>3</sub> nanolaminates by ALD have then been employed to understand structure/property relationships. Over the last three years, our work has concentrated on thermal and optical properties that are important for designing better thermal barrier protective coatings and enhanced x-ray mirrors. We aim to establish correlations between thermal and optical properties and nanolaminate structure, interfacial density and composition. We have fully characterized the ultralow thermal conductivity and ultrahigh x-ray reflectivity of W/Al<sub>2</sub>O<sub>3</sub> nanolaminates. These investigations are important for a basic understanding of nanolaminates and for many future applications of nanolaminate films.

## II. Research Topics

Our AFOSR effort has concentrated on a number of important topics during the course of this research. These topics include:

- Understanding the ultrahigh x-ray reflectivity from W/Al<sub>2</sub>O<sub>3</sub> nanolaminates. We have performed additional characterization of 16-bilayer W/Al<sub>2</sub>O<sub>3</sub> nanolaminates using transmission electron microscopy (TEM) and x-ray rocking curves.
- Examination of the nucleation and growth during W ALD on Al<sub>2</sub>O<sub>3</sub> using high resolution quartz crystal microbalance (QCM) studies. These QCM studies were complemented by atomic force microscope (AFM) studies following the nucleation and growth of the surface roughness of the W ALD films.

- Development of a model for W ALD on  $\text{Al}_2\text{O}_3$  that is consistent with the nucleation of W islands that then the coalescence of these W islands into a continuous W film.
- Theoretical simulations of nucleation and growth during W ALD on  $\text{Al}_2\text{O}_3$  to understand the relationship between the W ALD growth per cycle and the change in surface roughness of the W ALD film.
- Optimization of the growth of W/ $\text{Al}_2\text{O}_3$  nanolaminates. The quality of the W/ $\text{Al}_2\text{O}_3$  nanolaminates depends on a thorough knowledge of the nucleation of W ALD on  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  ALD on W during W/ $\text{Al}_2\text{O}_3$  nanolaminate growth. These studies were performed using in situ quartz crystal microbalance (QCM) measurements.
- X-ray reflectivity of W/ $\text{Al}_2\text{O}_3$  nanolaminates. We varied the W/ $\text{Al}_2\text{O}_3$  nanolaminate properties (number of bilayers, thickness of bilayers, relative thickness of two materials in the bilayer) to optimize the x-ray reflectivity. These studies made extensive use of our x-ray diffractometer obtained from the DURIP program.
- Examination of the nucleation and growth during W ALD on  $\text{Al}_2\text{O}_3$  using atomic force microscopy (AFM). We measured the surface roughness during the nucleation region. These measurements revealed a surface roughness that was consistent with the nucleation of islands that then coalesce into a continuous smooth film.
- Improvement of treatment of excess reactant and products during W ALD and  $\text{Al}_2\text{O}_3$  ALD. Pumping of these reactants and products seriously degrades vacuum pump performance. We evaluated a new burn box design that can chemically degrade the reactants and products before they reach the vacuum pumps.
- Thermal conductivity of the W/ $\text{Al}_2\text{O}_3$  nanolaminates. We have evaluated the thermal conductivity of W/ $\text{Al}_2\text{O}_3$  nanolaminates versus bilayer thickness in conjunction with Prof. David Cahill at the University of Illinois at Urbana.
- X-ray reflectivity of W/ $\text{Al}_2\text{O}_3$  nanolaminates. We examined the effect of the various W/ $\text{Al}_2\text{O}_3$  nanolaminate properties (number of bilayers, thickness of bilayers, relative thickness of two materials in the bilayer) to optimize the x-ray reflectivity.

In addition to these core topics, we also explored a number of additional topics including:

- New ALD surface chemistry for the growth of AlN and WN. These materials will be interesting in combination with  $\text{Al}_2\text{O}_3$  or W in nanolaminate structures.
- Transitions of ALD techniques to industry for various technological applications. We have worked with several collaborators to transition ALD techniques to various applications including microelectromechanical systems (MEMS).
- Development of new methods to use ALD to deposit laterally-graded multilayers for x-ray optical applications.

- Exploration of ALD on carbon nanotubes to insulate the carbon nanotubes and to define a carbon nanotube coaxial cable.
- Investigation of W and  $\text{Al}_2\text{O}_3$  ALD on polymers for possible applications such as flexible x-ray mirrors.

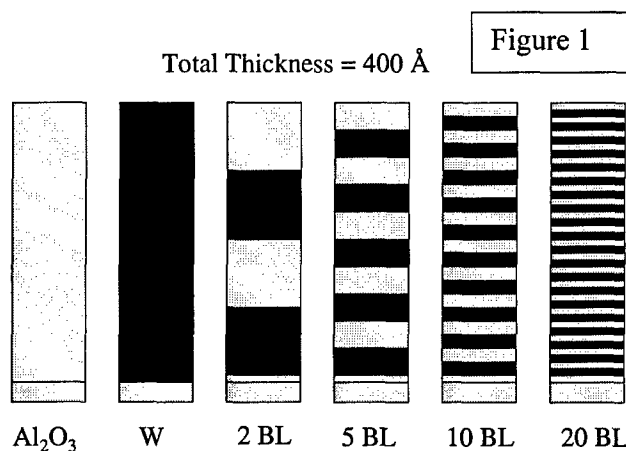
Our progress in studying these research topics over the last three years has been excellent. Our research effort has been headed by postdoctoral research associate Dr. Francois Fabreguette. He has been in charge of the  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates for x-ray mirrors and has been responsible for the characterization of the  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates using x-ray reflectivity (XRR) and TEM and the work on laterally graded multilayers. Francois has worked closely with a graduate student, Zachary Sechrist. Francois and Zach have worked together on the optimization of the  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates for x-ray mirrors. Francois has also worked closely with Dr. Rikard Wind. Dr. Wind is a postdoctoral research associate who is working on the QCM studies of  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminate growth and also performing the theoretical simulations of W ALD on  $\text{Al}_2\text{O}_3$ .

We have also explored some additional topics outside of our core research on  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates. Some of this work was performed by graduate student, Chris Wilson. Chris has examined  $\text{Al}_2\text{O}_3$  ALD and W ALD on various polymers. Additional work was performed by another postdoctoral research associate, Cari Herrmann. Cari was largely responsible for various fruitful applications of ALD with our many collaborations. Many of these collaborations have focused on ALD on MEMS and ALD on carbon nanotubes.

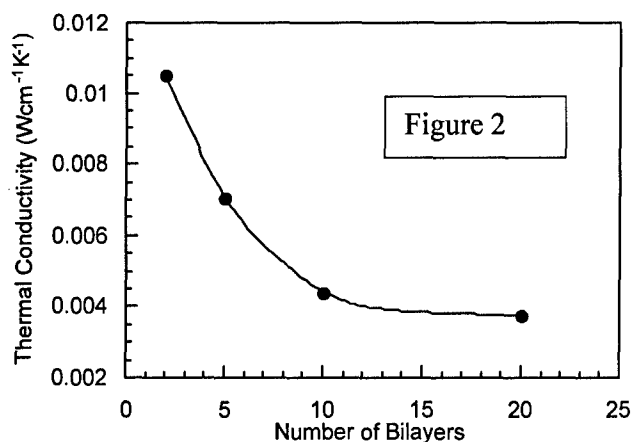
### III. Accomplishments/ New Findings

One key accomplishment of this research was our growth of  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates with various bilayer thicknesses and the measurement of their thermal conductivity by Prof. David Cahill at the University of Illinois at Urbana. A number of films with a thickness of 400 Å were grown with different number of bilayers (BL) as shown in Figure 1.

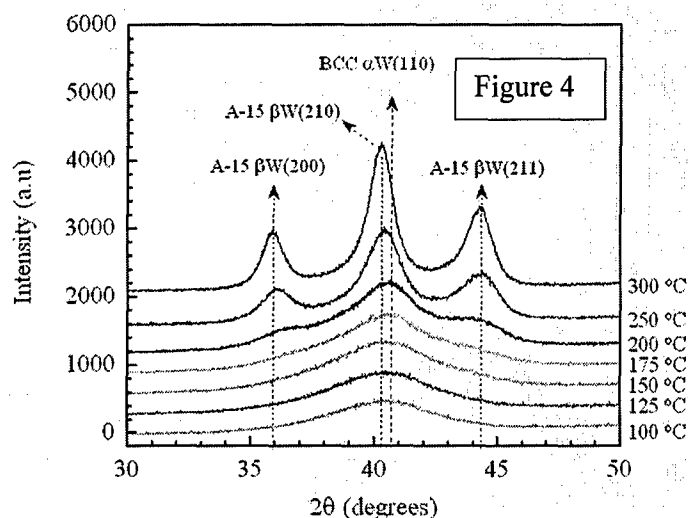
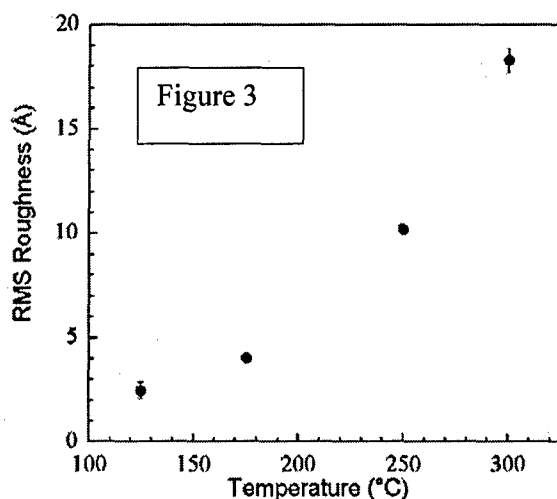
The thermal conductivity was then measured to determine the effect of interfacial density on thermal conductivity. The results



of the thermal conductivity measurements are shown in Figure 2. The thermal conductivity was reduced dramatically versus number of bilayers. These results were very significant because they illustrated the importance of interfacial density for thermal conductivity. In addition, the magnitude of the thermal conductivity was very low.  $\text{ZrO}_2$  has the lowest known thermal conductivity for a refractory inorganic material of  $\sim 0.01 \text{ Wcm}^{-1}\text{K}^{-1}$ . The lowest thermal conductivity for the  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminate is almost a factor of x3 lower. This low thermal conductivity could be important for future thermal barrier coatings.



Another key accomplishment from this research was our optimization of the x-ray reflectivity from  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates. We knew from our previous work that high x-ray reflectivities could be obtained from  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates deposited at  $177^\circ\text{C}$ . We initially measured a reflectivity of 67% for  $\lambda = 1.54 \text{ \AA}$  from the  $\text{CuK}\alpha$  transition. Since this result was obtained without any knowledge of the optimum parameters for an x-ray mirror, we were confident that we could improve on this reflectivity after we understood the factors that dictate x-ray reflectivity.

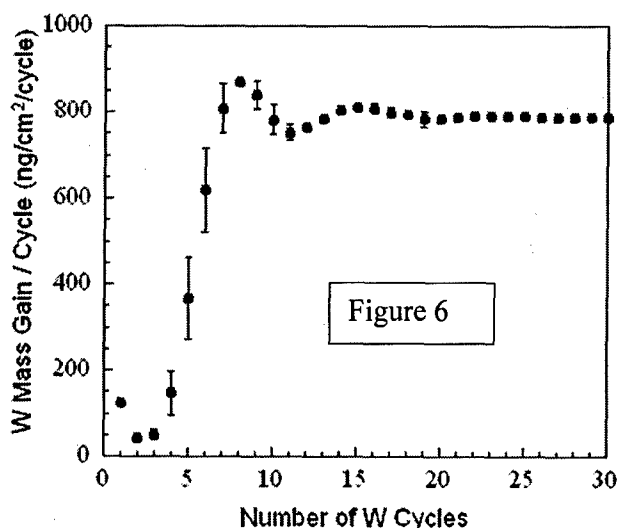
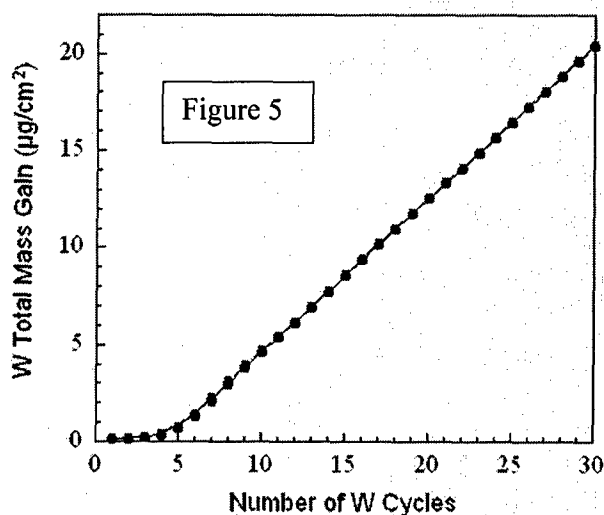


One of important parameters for x-ray reflectivity is the interfacial roughness in the superlattice structure. To minimize the interfacial roughness to maximize the reflectivity, we examined the surface roughness of  $\text{W}$  ALD films versus growth temperature. We determined that lower growth temperatures yield much lower surface roughnesses. A summary of surface roughness versus growth temperature

during W ALD is shown in Figure 3. Based on these results, we determined that the W ALD nanolayers in the W/Al<sub>2</sub>O<sub>3</sub> nanolaminates needed to be grown at 125°C.

The change of W ALD growth temperature from 177°C to 125°C also led to interesting changes in the W crystal structure. The W ALD films grown at higher temperatures  $\geq 200^\circ\text{C}$  displayed three diffraction peaks consistent with lower density,  $\beta$ -tungsten (14.6 g/cm<sup>3</sup>). In contrast, W ALD films grown at lower temperatures  $\leq 150^\circ\text{C}$  displayed a single diffraction peak consistent with higher density  $\alpha$ -tungsten (19.3 g/cm<sup>3</sup>). This change in crystal structure is displayed in Figure 4. This discovery was relevant to the optimization of the x-ray mirror reflectivity because the x-ray reflectivity is dependent on the density difference between the two layers in the superlattice. The larger the density difference, the higher the x-ray reflectivity. Consequently, we determined that the lower temperatures  $<150^\circ\text{C}$  were important both for lower surface roughness and higher density W ALD films.

After determining that the W/Al<sub>2</sub>O<sub>3</sub> nanolaminates needed to be grown at 125°C, we reoptimized the nucleation and growth during W ALD on Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> ALD on W using in situ quartz crystal microbalance (QCM) experiments. The nucleation was optimized by studying the effect of the parameters for the WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> reactant exposures (pressure and time) during W ALD on the nucleation behavior. Optimization of these



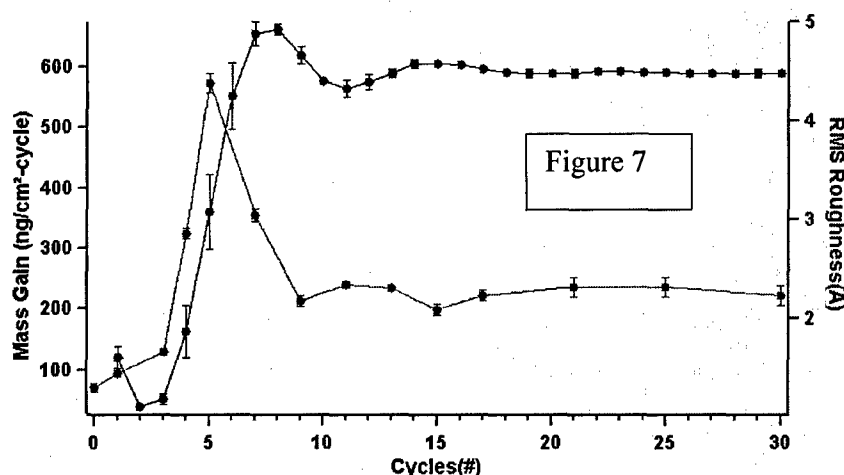
parameters led the best nucleation of W ALD shown in Figure 5. Even under the best conditions, 4-5 WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> cycles are required to nucleate the W ALD and obtain linear growth.

The mass gain during each WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> cycle reveals interesting detail about the W ALD nucleation. Figure 6 shows the W mass gain per WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> cycle. Notice that the mass gain per cycle increases dramatically after 3 WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> cycles. The mass gain per cycle then overshoots and “rings”

down after 15-20 WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> cycles. This interesting oscillatory behavior is very reproducible.

We believe that these data can be used to model the nucleation and growth of W ALD on  $\text{Al}_2\text{O}_3$ . This topic is extremely important for a basic understanding of ALD.

The W mass gain per cycle suggests that W ALD nucleates as islands after  $\sim 3$   $\text{WF}_6/\text{Si}_2\text{H}_6$  cycles. The islands then progressively grow during cycles 4-8. By cycle 8, the W mass gain per cycle reaches a peak and then decreases. This puzzling behavior can be explained in terms of surface roughness. The islands are rough and will display the highest W mass gain per cycle at the moment where the islands have grown together with each other to create a continuous film. Further W ALD will then smooth the surface roughness and lead to a reduced W mass gain per cycle.



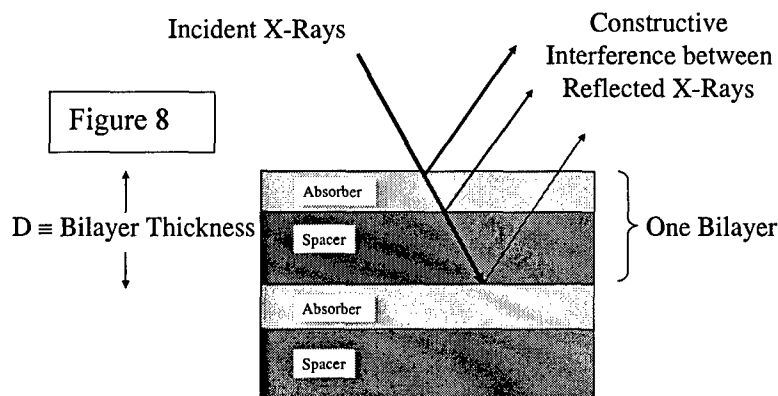
To test this idea about the existence of W islands and surface roughness, the W ALD layer on  $\text{Al}_2\text{O}_3$  was examined with atomic force microscopy (AFM) after different numbers of  $\text{WF}_6/\text{Si}_2\text{H}_6$  cycles. If the islands exist during the initial stages of W ALD growth on  $\text{Al}_2\text{O}_3$ , then these islands should lead to increased surface roughness. The AFM measurements confirmed that the roughest surface was obtained during the region of rapid increase of W mass gain per cycle. This correlation is shown in Figure 7. We also have modeled this data to further develop our understanding of W ALD on  $\text{Al}_2\text{O}_3$ . We note that these are the most detailed measurements of nucleation and growth during ALD for any system to date.

Based on these QCM and AFM studies, we realized that the smoothest W ALD films will be obtained after 11  $\text{WF}_6/\text{Si}_2\text{H}_6$  cycles. The requirement to utilize 11  $\text{WF}_6/\text{Si}_2\text{H}_6$  cycles places some restrictions on the minimum W ALD layer thickness that can be employed for the Bragg reflector based on the W/ $\text{Al}_2\text{O}_3$  nanolaminate. We then set out to optimize the reflectivity of the W/ $\text{Al}_2\text{O}_3$  superlattice as an x-ray mirror for hard x-rays at 1.54 Å.

The reflectivity of a Bragg mirror reflector is dependent on a superlattice structure of absorber and spacer layers. A bilayer is one absorber/spacer layer characterized by  $D$ , the bilayer thickness and  $\gamma$ , the spacer fraction defined by the spacer thickness divided by  $D$ . Figure 8 shows these various parameters that define the Bragg reflector.



These results from both the reflectivity measurements versus spacer fraction at constant bilayer thickness and versus bilayer thickness at constant spacer fraction allowed us to confirm the expected behavior of the x-ray reflectivity on these two key parameters. After confirming this expected behavior, a much larger superlattice was grown to obtain the highest possible x-ray



$$\gamma = \text{Spacer Thickness}/D \equiv \text{Spacer Fraction}$$

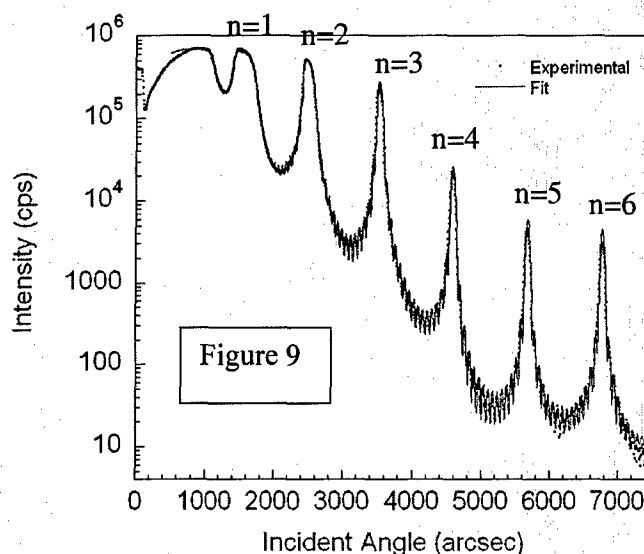
Bragg peak is nearly equal to the total beam intensity. The total beam intensity is obtained at the critical angle. The critical angle occurs just before the x-rays begin to penetrate into the underlying substrate. At angles less than the critical angle, the x-rays undergo complete external reflection. This superlattice was grown to obtain  $\gamma=0.72$  and  $D=122\text{\AA}$ . The x-ray reflectivity measurements yielded  $\gamma=0.76$ ,  $D=142\text{\AA}$ .

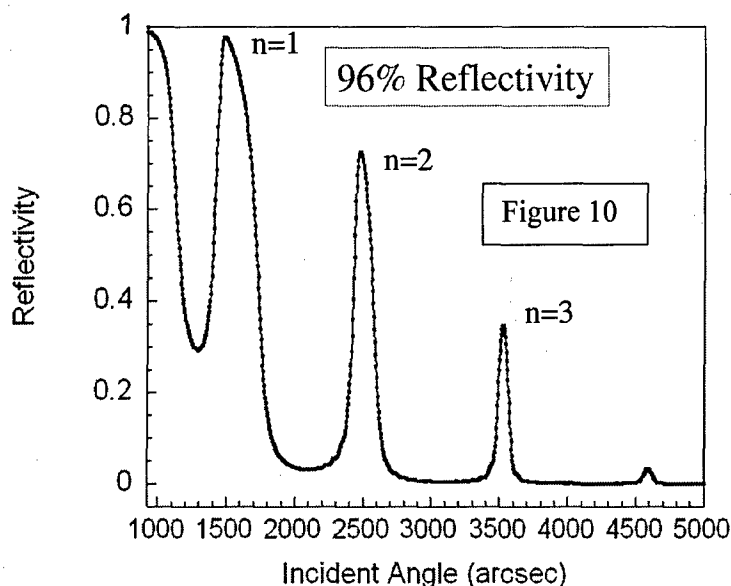
The high reflectivity of this 16-bilayer superlattice is most dramatically revealed by a plot of the linear reflected intensity versus the incident angle. This plot is shown in Figure 10. The reflectivity of the  $n=1$  Bragg peak is 96%. This reflectivity of 96% is the highest reflectivity ever reported for Bragg reflectors at  $1.54\text{\AA}$ . The reflectivity for the  $n=2$  and  $n=3$  Bragg peaks is also exceptional. These high reflectivities for higher order Bragg peaks are only observed from exceptional superlattice structures.

The x-ray reflectivity for the  $\text{CuK}\alpha$  line at  $1.54\text{\AA}$  is important because hard x-rays are used for a variety of analytical purposes to characterize crystal structure and to determine the characteristics of thin films using x-ray reflectivity measurements. The  $\text{CuK}\alpha$  line is one of the dominant x-ray wavelengths used for x-ray analysis. The Lawrence Berkeley Laboratory keeps

reflectivity. This larger superlattice was composed of 16 bilayers.

The optimized 16-bilayer superlattice displayed very high reflectivity. The logarithm of the reflected intensity versus incident angle is shown in Figure 9. The reflectivity for the  $n=1$





a website that documents the best reflectivity for the  $\text{CuK}\alpha$  line. Our reflectivity of 96% places our 16-bilayer  $\text{W}/\text{Al}_2\text{O}_3$  superlattice at the top of the list with the best reflectivity ever reported for x-ray reflectivity for  $1.54 \text{ \AA}$ .

Figure 11 shows a cross-sectional transmission electron microscopy (TEM) image of the  $\text{W}/\text{Al}_2\text{O}_3$  multilayer. This TEM image illustrates the structural integrity of the  $\text{W}/\text{Al}_2\text{O}_3$

multilayer where the dark thin layers are the W ALD absorber layers and the thick lighter layers are the  $\text{Al}_2\text{O}_3$  ALD spacer layers. The first eight bilayers are perfectly conformal to the underlying  $\text{Si}(100)$  substrate. The top bilayers show some roughness that replicates the roughness in the underlying bilayers.

The roughness on the top of the  $\text{W}/\text{Al}_2\text{O}_3$  multilayer is believed to result primarily from the W crystallinity. This roughness is correlated and propagates through the whole  $\text{W}/\text{Al}_2\text{O}_3$  multilayer. This correlated roughness should not seriously affect the specular reflectivity at the Bragg peak. The inset in Figure 11 shows a high resolution TEM image of the  $\text{W}/\text{Al}_2\text{O}_3$  multilayer. This TEM image illustrates the sharp interfaces between the W and  $\text{Al}_2\text{O}_3$  layers and confirms the thicknesses for the spacer layer and W absorber layer.

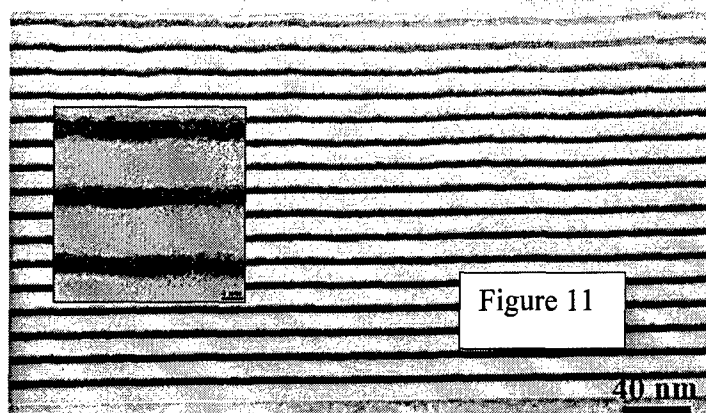
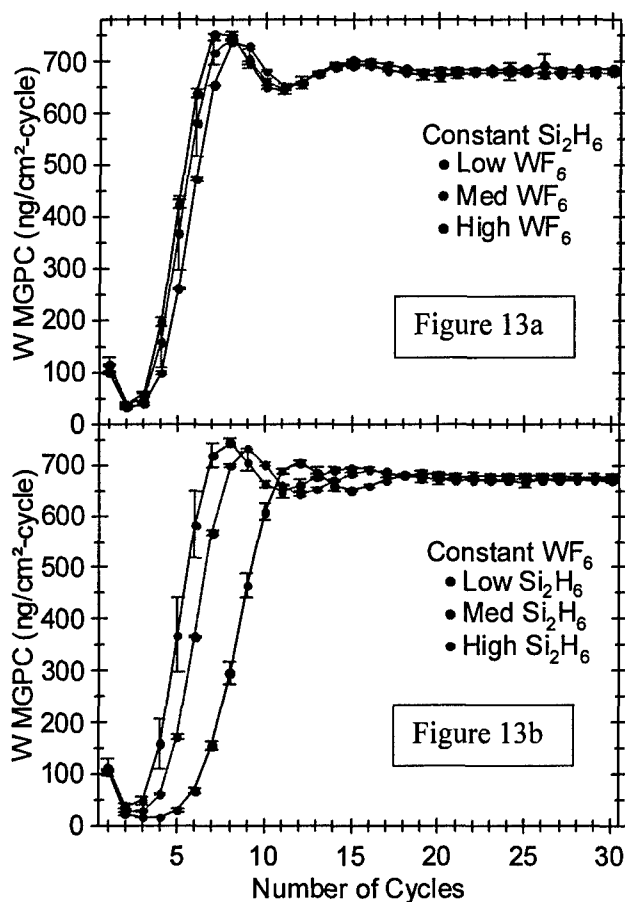
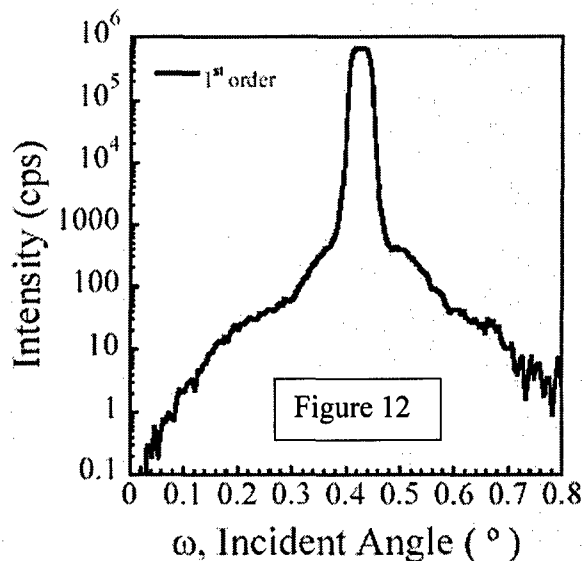


Figure 11

An off-specular transverse scan at the first-order Bragg peak is shown in Figure 12. This rocking curve is obtained by stopping the  $\omega, 2\theta$  scan at the maximum reflectivity. The incident angle,  $\omega$ , is then "rocked" while keeping the detector fixed at the initial Bragg condition. Figure 3 displays a sharp specular component when the incident angle,  $\omega$ , reaches the Bragg condition. The peak occurs at an incident angle of approximately  $0.42^\circ$ . The specular component is on top of a diffuse background that is caused by both the correlated and uncorrelated interfacial roughnesses. For the  $\text{W}/\text{Al}_2\text{O}_3$  multilayers, the ratio is  $\sim 10,000$ . This ratio is comparable or

higher than the ratio of  $\sim 5,000$  reported for the best multilayer x-ray mirrors with low interfacial roughness.

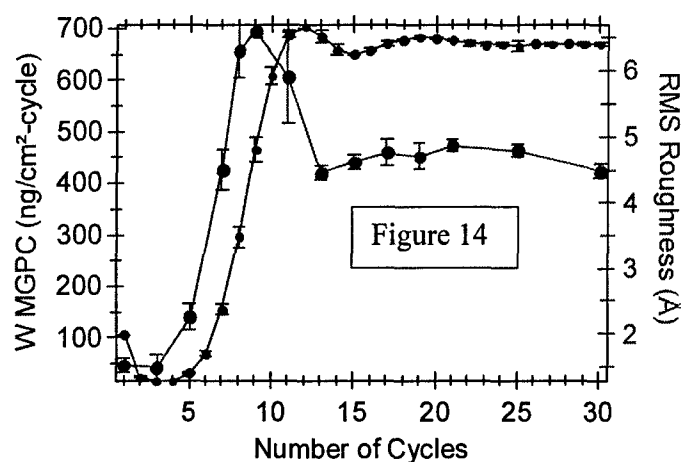
The high x-ray reflectivity obtained by ALD techniques is attributed to the precise bilayer thicknesses and ultra-smooth interfaces obtained by ALD. The atomic level control of growth during ALD produces precise bilayer thicknesses. The self-limiting surface chemistry during ALD ensures that every surface reaction goes to completion. This ALD growth mechanism prevents randomness in the deposition process that can produce interfacial roughness. In contrast, the stochastic nature of the deposition process during PVD can lead to more interfacial roughness depending on the growth mechanism.



Some interfacial roughness may result during ALD from nucleation difficulties or film crystallinity. However, the nucleation can be optimized by tuning the reaction conditions and the film crystallinity can be reduced by lowering the growth temperature. Because of the excellent conformality of the ALD process, any roughness in the multilayer will occur as correlated roughness. Correlated roughness is much less detrimental to specular reflectivity at the Bragg peak than uncorrelated roughness.

The growth of the  $W/Al_2O_3$  nanolaminates is critically dependent on the nucleation and growth of the individual W and  $Al_2O_3$  layers.  $Al_2O_3$  ALD nucleates readily on the W nanolayer. However, W ALD has nucleation difficulties on the  $Al_2O_3$  nanolayer. To understand the growth of the  $W/Al_2O_3$  nanolaminate, we have explored the details of the W ALD nucleation on  $Al_2O_3$  using QCM studies.

Figure 13 shows the W ALD mass gain per cycle (MGPC). This W ALD MGPC shows a distinct "ringing" behavior that reveals information about the underlying nucleation and growth mechanism. The "ringing" is always observed but can be shifted depending on the reaction conditions. The  $\text{WF}_6$  exposures have little effect on this "ringing" as shown in Figure 13a. However, the  $\text{Si}_2\text{H}_6$  exposures will shift the position of the "ringing" as shown in Figure 13b.

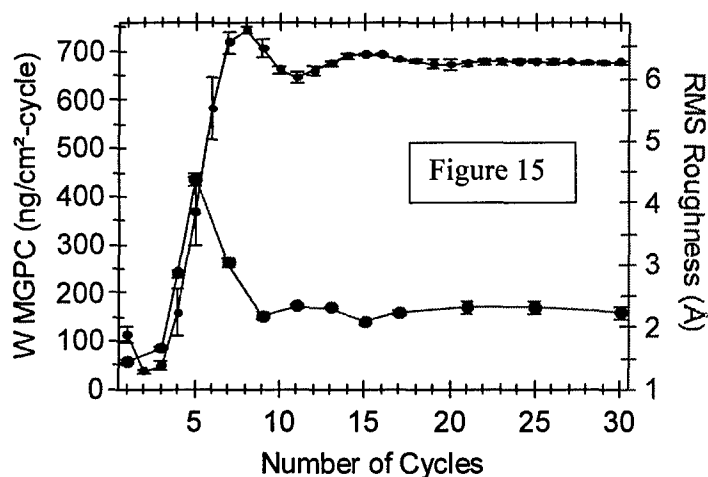


The low  $\text{Si}_2\text{H}_6$  exposures require more cycles for nucleation.

These QCM results are in agreement with three-dimensional W island growth that produces a maximum in the W ALD MGPC. This maximum corresponds to the largest W surface area prior to the coalescence of the W islands.

The growth of W islands is also revealed by atomic force microscope measurements of

RMS roughness in Figure 14. The maximum roughness at low  $\text{Si}_2\text{H}_6$  exposure is observed after 9 cycles as the W islands are reaching their largest surface area prior to coalescence.

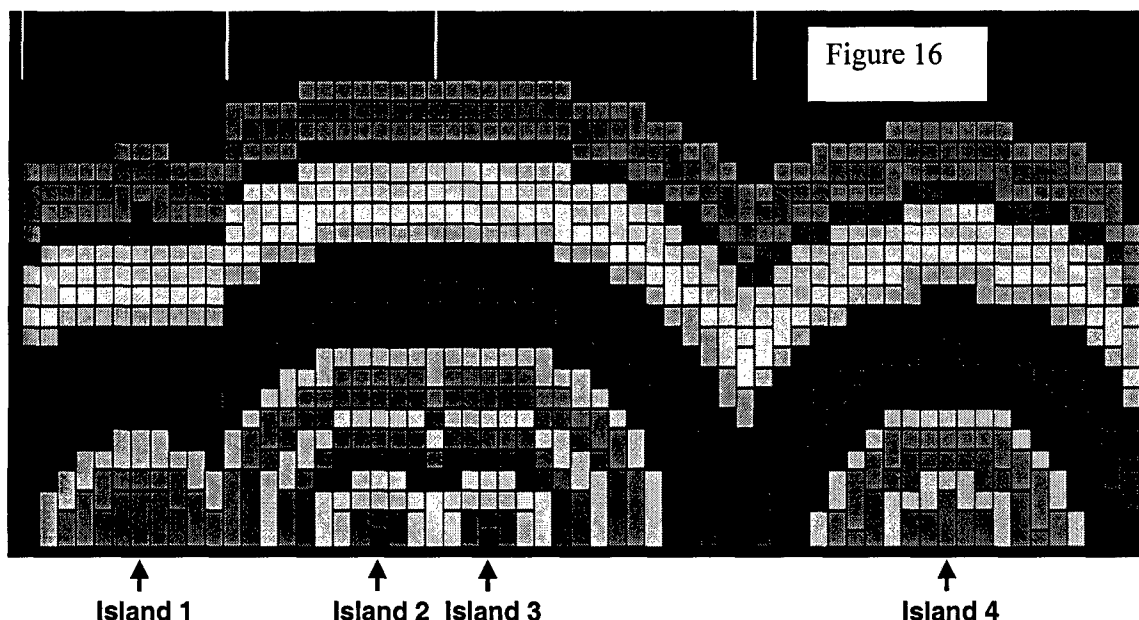


We have explored the effect of the various reaction parameters on the W ALD MGPC and the surface roughness. We find that the smoothest W ALD films are fabricated using the high  $\text{Si}_2\text{H}_6$  reactant exposures. The lower RMS surface roughness obtained with the higher  $\text{Si}_2\text{H}_6$  exposures is shown in Figure 15. The best x-ray mirrors are obtained using these higher  $\text{Si}_2\text{H}_6$  exposures.

We have excellent QCM data to use to test various models for the nucleation and growth of W ALD on  $\text{Al}_2\text{O}_3$ . The initial peak in the W ALD MGPC is attributed to the higher surface area of the W ALD film just prior to the coalescence of the W islands. One-dimensional and two-dimensional modeling has been performed to simulate the W ALD nucleation and growth. The increasing roughness with number of AB cycles can be understood in terms of initial

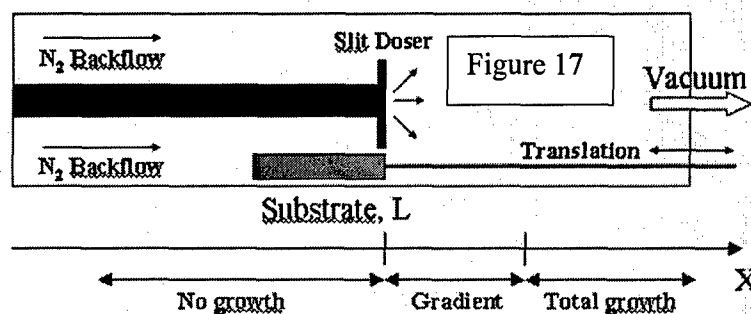
expansion of circles or spheres. One of these simulations is shown in Figure 16. Colors indicate the time evolution from red to blue and then the repetition of this same progression. Four islands are nucleated randomly in time. After the initial peak in surface roughness, the film progressively smooths as the islands grow together.

Many applications of the W/Al<sub>2</sub>O<sub>3</sub> nanolaminates for x-ray optics, such as x-ray lasers

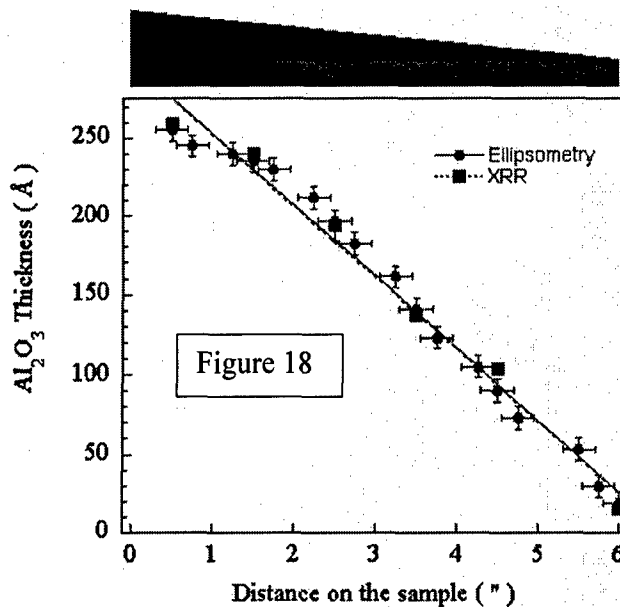


and x-ray microscopes, may require a laterally-graded multilayer. Laterally graded multilayers have a bilayer spacing that continuously changes versus spatial position. These graded multilayer structures are important for x-ray collimation and x-ray focusing. To obtain laterally graded W/Al<sub>2</sub>O<sub>3</sub> multilayers, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate.

Laterally graded multilayers can be fabricated using a slit doser to localize reactant delivery in a viscous flow gas stream. The substrate is then translated relative to the slit doser with a magnetic linear translator as displayed in Figure 17. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate.

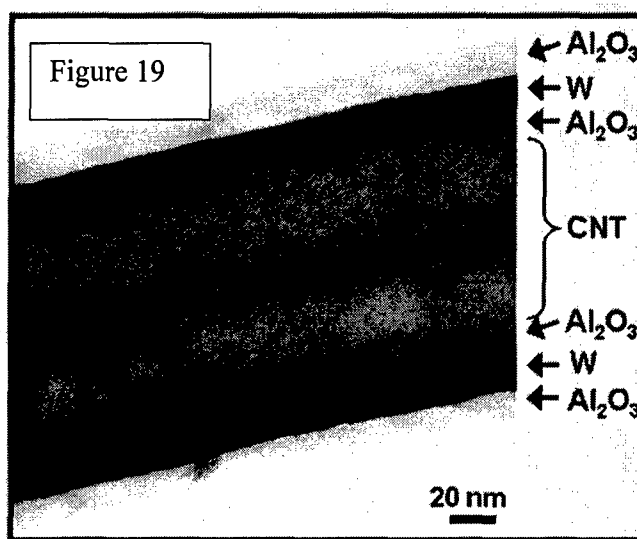


A laterally graded  $\text{Al}_2\text{O}_3$  ALD film was initially demonstrated by translating the substrate relative to the slit doser during  $\text{Al}_2\text{O}_3$  ALD reaction cycles. The variable angle ellipsometry and XRR results in Figure 18 quantified a varying  $\text{Al}_2\text{O}_3$  film thickness grown on a Si(100) wafer with a length of 6 inches. Changes in leakage current density and capacitance confirmed the  $\text{Al}_2\text{O}_3$  thickness gradient. In addition, a laterally graded  $\text{ZnO}/\text{Al}_2\text{O}_3$  multilayer was grown and characterized using XRR. The angle of the first Bragg peak revealed a bilayer spacing that changed as expected versus spatial position. This work on laterally-graded multilayers is just beginning and will be developed further in the continuation of our AFOSR research.



In addition to our core research on  $\text{W}/\text{Al}_2\text{O}_3$  nanolaminates, nucleation and growth during ALD and fabrication of designer multilayers for various technological applications, we have also worked on a variety of other ALD applications. We have started a new project on ALD on polymers. We have demonstrated  $\text{Al}_2\text{O}_3$  ALD on various polymer films and polymer particles. We have also collaborated with a number of outside groups on ALD applications. We have continued to work on applications of ALD for microelectromechanical systems (MEMS). We have also demonstrated ALD on carbon nanotubes. Both of these collaborations have been very fruitful and have led to interesting results and publications.

The application of ALD on carbon nanotubes is especially interesting since carbon nanotubes are being proposed for a variety of technological applications. In most cases, the applications require that the carbon nanotube be functionalized to obtain a particular property. We have demonstrated that multi-walled carbon nanotubes can easily be coated with  $\text{Al}_2\text{O}_3$  ALD. The  $\text{Al}_2\text{O}_3$  ALD can then act as a starting layer for important



multilayer structures. For example, W ALD can be deposited on the  $\text{Al}_2\text{O}_3$  ALD layer to form a conducting layer. Subsequently, an additional  $\text{Al}_2\text{O}_3$  ALD layer can be deposited on the W ALD layer to form an additional insulating layer. This  $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$  layer on the carbon nanotube would create a "carbon nanotube coaxial cable". A transmission electron micrograph (TEM) of a multi-walled carbon nanotube coated with a  $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$  layer is shown in Figure 19. This TEM image was obtained by our collaborators at NIST-Boulder.

#### IV. Personnel Supported

##### *Faculty*

1. Prof. Steven M. George (One Month Summer Salary)

##### *Postdoctoral Research Associates*

1. Dr. Francois Fabreguette
2. Dr. Rikard Wind

##### *Graduate Students*

1. Zachary Sechrist
1. Chris Wilson

#### V. Publications

Many manuscripts describing our AFOSR-supported research and collaborations involving our AFOSR-supported research have been published during the last three years.

1. N.D. Hoivik, J.W. Elam, R.J. Linderman, V.M. Bright, S.M. George and Y.C. Lee, "Atomic Layer Deposited Protective Coatings for Micro-Electromechanical Systems", *Sensor Actuat. A* **103**, 100-108 (2003).
2. J.W. Elam and S.M. George, "Growth of  $\text{ZnO}/\text{Al}_2\text{O}_3$  Alloy Films Using Atomic Layer Deposition", *Chem. Mater.* **15**, 1020-1028 (2003).
3. J.W. Elam, D. Routkevitch and S.M. George, "Properties of  $\text{ZnO}/\text{Al}_2\text{O}_3$  Alloy Films Grown Using Atomic Layer Deposition Techniques", *J. Electrochem. Soc.* **150**, G339-G347 (2003).
4. K. Gall, M. Hulse, M.L. Dunn, D. Finch, S.M. George and B.A. Corff, "Thermo-Mechanical Response of Bare and  $\text{Al}_2\text{O}_3$  Nanocoated Au/Si Bilayer Beams for MEMS", *J. Mater. Res.* **18**, 1575-1587 (2003).
5. T.M. Mayer, J.W. Elam, S.M. George and P.G. Kotula, "Atomic Layer Deposition of Wear-Resistant Coatings for Micromechanical Devices", *Appl. Phys. Lett.* **82**, 2883-2885 (2003).

6. M.D. Groner and S.M. George, "High-k Dielectrics Grown by Atomic Layer Deposition: Capacitor and Gate Applications" Chapter 10 in Interlayer Dielectrics for Semiconductor Technologies. Murarka, Eizenbert and Sinha, Eds., Elsevier Inc., pp. 327-348.
7. J.W. Elam, D. Routkevitch, P.P. Markilovich and S.M. George, "Conformal Coating on Ultrahigh-Aspect-Ratio Nanopores of Anodic Alumina by Atomic Layer Deposition", *Chem. Mater.* **15**, 3507-3517 (2003).
8. M.N. Rocklein and S.M. George, "Temperature-Induced Apparent Mass Changes Observed during Quartz Crystal Microbalance Measurements of Atomic Layer Deposition", *Anal. Chem.* **75**, 4975-4982 (2003).
9. K. Gall, M. L. Dunn, M. Hulse, D. Finch and S. M. George, "Effect of Al<sub>2</sub>O<sub>3</sub> Nanocoatings on the Thermo-Mechanical Behavior of Au/Si MEMS Structures", Conference Proceedings of the IEEE International Reliability Physics Symposium, Dallas, Texas, March 30-April 4, 2003, pp. 463-472.
10. R.K. Grubbs, J.W. Elam, C.E. Nelson and S.M. George, "Nucleation and Growth During Tungsten ALD on Al<sub>2</sub>O<sub>3</sub> Surfaces and Al<sub>2</sub>O<sub>3</sub> ALD on Tungsten Surfaces", *Thin Solid Films* **467**, 16-27 (2004).
11. M.D. Groner, F.H. Fabreguette, J.W. Elam and S.M. George, "Low Temperature Al<sub>2</sub>O<sub>3</sub> Atomic Layer Deposition", *Chem. Mater.* **16**, 639-645 (2004).
12. R.K. Grubbs, N.J. Steinmetz and S.M. George, "Gas Phase Reaction Products during Tungsten Atomic Layer Deposition Using WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub>", *J. Vac. Sci. Technol. B* **22**, 1811-1821 (2004).
13. R.M. Costescu, D.G. Cahill, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Preparation of Ultra-Low Thermal Conductivity W/Al<sub>2</sub>O<sub>3</sub> Nanolaminates", *Science* **303**, 989-990 (2004).
14. Y. Zhang, M.L. Dunn, K. Gall, J.W. Elam and S.M. George, "Suppression of Inelastic Deformation of Nanocoated Thin Film Microstructures", *J. Appl. Phys.* **95**, 8216-8225 (2004).
15. Z.A. Sechrist, F.H. Fabreguette, O. Heintz, T.M. Phung, D.C. Johnson and S.M. George, "Optimization and Structural Characterization of W/Al<sub>2</sub>O<sub>3</sub> Nanolaminates Grown Using Atomic Layer Deposition Techniques", *Chem. Mater.* **17**, 3475-3485 (2005).
16. F.H. Fabreguette, Z.A. Sechrist, J.W. Elam and S.M. George, "Quartz Crystal Microbalance Study of Tungsten Atomic Layer Deposition using WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub>", *Thin Solid Films* **488**, 103-110 (2005).
17. C.F. Herrmann, F.W. DelRio, V.M. Bright and S.M. George, "Conformal Hydrophobic Coatings Prepared Using Atomic Layer Deposition Seed Layers and Non-Chlorinated Hydrophobic Precursors", *J. Micromech. Microeng.* **15**, 984-992 (2005).



18. C.F. Herrmann, F.W. DelRio, S.M. George and V.M. Bright, "Properties of Atomic Layer Deposited  $\text{Al}_2\text{O}_3/\text{ZnO}$  Dielectric Films Grown at Low Temperature for RF MEMS", *Proceedings of SPIE* **5715**, 159-166 (2005).
19. M.K. Tripp, F.H. Fabreguette, C.H. Herrmann, S.M. George and V.M. Bright, "Multilayer Coating Technique to Enhance X-Ray Reflectivity of Polysilicon Micro-Mirrors at 1.54 Å Wavelength", *Proceedings of SPIE* **5720**, 241-251 (2005).
20. D.C. Miller, C.F. Herrmann, H.J. Maier, S.M. George, C.R. Stoldt and K. Gall, "Intrinsic Stress Development and Microstructure Evolution of Au/Cr/Si Multilayer Thin Films Subject to Annealing", *Scripta Materialia* **52**, 873-879 (2005).
21. S.W. Kang, S.W. Rhee and S.M. George, "Infrared Spectroscopic Study of Atomic Layer Deposition (ALD) Mechanism for Hafnium Silicate Thin Films Using  $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]$  and  $\text{H}_2\text{O}$ ", *J. Vac. Sci. Technol. A* **22**, 2392-2397 (2004).
22. M.J. Pellin, P.C. Stair, G. Xiong, J.W. Elam, J. Birrell, L. Curtiss, S.M. George, C.Y. Han, L. Iton, H. Kung, M. Kung and H.H. Wang, *Catalysis Letters* **102**, 127-130 (2005).
23. C.A. Wilson, R.K. Grubbs and S.M. George, "Nucleation and Growth during  $\text{Al}_2\text{O}_3$  Atomic Layer Deposition on Polymers", *Chem. Mater.* **17**, 5625 (2005).
24. C.F. Herrmann, F.H. Fabreguette, D.S. Finch, R. Geiss and S.M. George, "Multilayer and Functional Coatings on Carbon Nanotubes Using Atomic Layer Deposition", *Appl. Phys. Lett.* **87**, 123110 (2005).
25. F.H. Fabreguette, R.W. Wind and S.M. George, "Ultra-high X-Ray Reflectivity from  $\text{W}/\text{Al}_2\text{O}_3$  Multilayers Fabricated Using Atomic Layer Deposition", *Appl. Phys. Lett.* **88**, 013116 (2006).

## VI. Interactions/ Transitions

The results from our AFOSR-sponsored research on ALD and nanolaminates grown using ALD are technologically relevant. Atomic layer deposition (ALD) techniques have many useful industrial applications. In the past, our results have been implemented by the semiconductor industry. The most prominent example is W ALD. We initially developed W ALD to fabricate  $\text{Al}_2\text{O}_3/\text{W}$  ceramic/metal nanolaminates for superior thermal barrier coatings. Our W ALD process is now being used for contact hole filling. The self-limiting surface chemistry that we developed for W ALD is used by Applied Materials (Sunnyvale, Calif.) and Novellus (San Jose, Calif.) as a W seed in contact holes for W chemical vapor deposition (CVD). W CVD is used to fill the contact holes in the first level of backend interconnects.

Our ALD-supported by AFOSR has also found many applications for MEMS. We have collaborations with several groups in the Mechanical Engineering Department and CAMPmode at the University of Colorado. This work has been very productive. Over the first two years of this AFOSR grant, CAMPmode supported a postdoctoral research associate, Dr. Cari Herrmann,

who was dedicated to ALD for MEMS applications. Part of Cari's research focused on a collaborative MEMS project with the Air Force Research Laboratory in Dayton, Ohio. In addition, we had a two year collaboration with Sandia National Laboratory in Albuquerque, New Mexico. Sandia funded a part time (2/3) postdoctoral research associate, Dr. Rikard Wind, to investigate the mechanical properties of ALD films for potential MEMS applications.

Over the last three years, we also have deposited a variety of ALD films on different devices and substrates for various industries. A list of our collaborations is given below. Some of these collaborations have led to direct industrial funding and others have led to Phase I or Phase II SBIR funding or in-kind support including equipment donations.

**A. Intel Corporation (through the NSF-sponsored Ceramic and Composite Materials Center at the University of New Mexico).** Intel Corporation is interested in diffusion barriers for copper interconnects and copper seeds for copper electrodeposition for multilevel interconnects. This collaboration has been funded by Intel membership in the NSF-sponsored Ceramic and Composite Materials Center at the University of New Mexico. This research utilizes one of the viscous flow ALD reactors that we developed during our support from AFOSR.

**B. Advanced Energy.** Advanced Energy in Fort Collins, Colorado, is a maker of power supplies and plasmas sources for the semiconductor industry. Advanced Energy is very interested in plasma ALD. They have provided plasma sources to facilitate our exploration of plasma ALD over the past several years. One of these plasma sources was used on a project that focused on ALD coatings on energetic organic materials. This project has been sponsored by Eglin Air Force Base and more recently by Phase II STTR funding.

**C. Synkera.** Synkera is a startup in Longmont, Colorado, that is focused on various nanotechnologies. We worked with them on an Phase I SBIR program. This project focused depositing nanorods in anodic alumina membranes for infrared dome applications. The ALD surface chemistry for the target material for the nanorods, AlN, was developed during our previous support from AFOSR. This project began Phase II funding in September 2005.

**D. Genus, Inc.** Genus, Inc. in Sunnyvale, California, is a provider of equipment for semiconductor fabrication. In the last several years, Genus has concentrated on equipment for ALD. We have worked with Genus on the development of new ALD surface chemistries for the deposition of nitrides, such as AlN. This work utilizes the ALD viscous flow reactors that we have built for our AFOSR-supported research.

**E. ALD NanoSolutions.** ALD NanoSolutions is a startup founded by the PI and Prof. Al Weimer in the Dept. of Chemical and Biological Engineering at the University of Colorado. Earlier, we received support from ALD NanoSolutions through an Phase I STTR program entitled "ALD of Oxidizer Coatings on Aluminum Nanoparticles to Fabricate SuperThermite Explosives". This earlier research initiated our work on organic energetic materials that is now

partially supported by Eglin Air Force Base. In addition, a subcontract on the Phase II STTR contract to ALD NanoSolutions for the continuation of this work began in January 2005.

We also received support from ALD NanoSolutions over the last year to demonstrate W ALD on Co nanoparticles and polycarbonate particles. The W ALD on Co nanoparticles is needed to protect small Co nanoparticles from oxidation. These Co nanoparticles are used to make WC/Co hard coatings. W ALD on polycarbonate particles may be useful to make conducting polymers that are effective for reduction of electromagnetic interference (EMI). ALD NanoSolutions has a strategic partnership with the OM Group in Cleveland, Ohio, that is supporting this research. The W ALD was developed during our earlier support from AFOSR.

**F. Hewlett Packard.** We have continued to collaborate with Hewlett Packard in Corvallis, Oregon to deposit tungsten on various MEMS structures using W ALD. These MEMS structures are for inkjet printers. The W ALD was developed during our earlier support from AFOSR.

**G. DuPont Research & Development.** Over the last two years, we received support from DuPont for two exploratory ALD projects. The first DuPont contract is funding a postdoctoral research associate to study the deposition of  $\text{Al}_2\text{O}_3$  ALD on two DuPont polymers, Kapton and polyethylene naphthalate (PEN). Both of these polymers are important for organic electronics and organic light emitting diodes (OLEDs). This project has demonstrated that the  $\text{Al}_2\text{O}_3$  ALD gas diffusion barrier helps to prevent  $\text{H}_2\text{O}$  and  $\text{O}_2$  gases from diffusing through the polymer substrate and reacting with the oxygen-sensitive parts of organic electronic devices. This project utilizes an ALD flow reactor whose design was developed in our earlier research supported by AFOSR.

The second DuPont contract funded a postdoctoral research associate to study Cu ALD using some new precursors developed by DuPont. This project was very exploratory and used an ALD flow reactor design that was developed in our earlier research supported by AFOSR. This project was conducted from January 2004 through January 2005.

**H. Ferro Electronic Material Systems.** We have received support from Ferro for studies of ALD on  $\text{BaTiO}_3$  particles for application in multilayer capacitors. This work utilized surface chemistries for ZnO and  $\text{SiO}_2$  ALD that were developed during our earlier AFOSR support.

The PI has been invited to discuss our AFOSR-supported research at many invited talks:

1. "Atomic Layer Deposition for Thin Film Growth", Analytical Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 23, 2002.
2. "Thin Film Growth Using Atomic Layer Deposition", Chemical Physics Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 27, 2002.

3. "Thin Film Growth Using Atomic Layer Deposition", Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina, October 7, 2002.
4. "Thin Film Growth Using Atomic Layer Deposition", Corporate Research and Development, The Dow Chemical Company, Midland, Michigan, November 11, 2002.
5. "Atomic Layer Deposition for Improved MEMS Reliability", Thin Film, Vacuum, and Packaging Department, Sandia National Laboratories, Albuquerque, New Mexico, January 16, 2003.
6. "Atomic Layer Deposition for Conformal Coating of High Aspect Ratio Structures", ICMI 2003 – Fourth International Conference on Microelectronics and Interfaces, American Vacuum Society, Santa Clara Convention Center, Santa Clara, California, March 4, 2003.
7. "Thin Film Growth Using Atomic Layer Deposition", Optoelectronic Computing Systems Seminar, Dept. of Electrical and Computer Engineering, University of Colorado, Boulder, Colorado, April 11, 2003.
8. "Fabricating Energetic SuperThermite Particles Using Atomic Layer Deposition Techniques", Technanogy, LLC, Santa Ana, California, May 19, 2003.
9. "Optimizing and Understanding Semiconductor Gas Sensors Using Atomic Layer Deposition Techniques", Nanomaterials Research LLC, Longmont, Colorado, May 23, 2003.
10. "Thin Film Growth Using Atomic Layer Deposition Techniques", Sporian Microsystems, Boulder, Colorado, May 27, 2003.
11. "Fabrication and Properties of  $\text{Al}_2\text{O}_3/\text{W}$  Nanolaminates Using Atomic Layer Deposition", ALD Symposium, Sandia National Laboratories, Albuquerque, New Mexico, July 28, 2003.
12. "Low Temperature Atomic Layer Deposition", Northern California American Vacuum Society Thin Films 2003 Annual Symposium, Silicon Valley Conference Center, San Jose, California, September 30, 2003.
13. "Atomic Layer Deposition on Polymers", Vitex Systems, San Jose, California, October 1, 2003.
14. "Low Temperature Atomic Layer Deposition", Genus, Inc., Sunnyvale, California, October 1, 2003.
15. "Incorporation and Control of Silica in Hafnium Silicates using Atomic Layer Deposition Techniques", Genus, Inc., Sunnyvale, California, October 1, 2003.
16. "Fabrication and Properties of Nanolaminates Using Atomic Layer Deposition Techniques", Analytical Chemistry Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, October 6, 2003.

17. "Atomic Layer Deposition of Metals", Advanced Metallization Conference (AMC) 2003, Workshop on *Atomic Layer Deposition- Key Enable for Sub-100nm IC Technology*, Hotel Omni Mont-Royal, Montreal, Canada, October 20, 2003.
18. "Low Temperature Atomic Layer Deposition", Northern California American Vacuum Society Thin Films 2003 Annual Symposium, Silicon Valley Conference Center, San Jose, California, September 30, 2003.
19. "Atomic Layer Deposition on Polymers", Vitex Systems, San Jose, California, October 1, 2003.
20. "Low Temperature Atomic Layer Deposition", Genus, Inc., Sunnyvale, California, October 1, 2003.
21. "Incorporation and Control of Silica in Hafnium Silicates using Atomic Layer Deposition Techniques", Genus, Inc., Sunnyvale, California, October 1, 2003.
22. "Fabrication and Properties of Nanolaminates Using Atomic Layer Deposition Techniques", Analytical Chemistry Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, October 6, 2003.
23. "Atomic Layer Deposition of Metals", Advanced Metallization Conference (AMC) 2003, Workshop on *Atomic Layer Deposition- Key Enable for Sub-100nm IC Technology*, Hotel Omni Mont-Royal, Montreal, Canada, October 20, 2003.
24. "Introduction to Atomic Layer Deposition", Honeywell, Specialty Chemicals, Buffalo, New York, January 19, 2003.
25. "Low Temperature Atomic Layer Deposition", Honeywell, Specialty Chemicals, Buffalo, New York, January 19, 2003.
26. "Atomic Layer Deposition of Metals", Honeywell, Specialty Chemicals, New York, January 19, 2003.
27. "Thin Film Growth Using Atomic Layer Deposition", *Surface Science 2004: 2<sup>nd</sup> Annual University of California Symposium on Surface Science and its Applications*, Department of Chemistry, University of California at San Diego, La Jolla, California, February 20, 2004.
28. "Al<sub>2</sub>O<sub>3</sub> Atomic Layer Deposition on Polymers", Symposium on Polymers in Micro- and Nano-electronics, Division of Polymeric Materials, 227<sup>th</sup> American Chemical Society National Meeting, Anaheim, California, March 31, 2004.
29. "Thin Film Growth Using Atomic Layer Deposition", *Engineering Leading Edge Program*, Micron Technology, Inc., Boise, Idaho, May 14, 2004.
30. "Thin Film Growth Using Atomic Layer Deposition", Department of Chemistry, University of Florida, Gainesville, Florida, July 6, 2004.

31. "Fabrication and Properties of  $\text{Al}_2\text{O}_3/\text{W}$  Nanolaminates Prepared Using Atomic Layer Deposition Techniques", *Annual Symposium of the Rocky Mountain American Vacuum Society*, Ben Parker Student Center, Colorado School of Mines, Golden, Colorado, August 12, 2004.
32. "Atomic Layer Deposition on Polymers", *American Vacuum Society Topical Conference on Atomic Layer Deposition (ALD2004)*, University of Helsinki, Helsinki, Finland, August 16 or 17, 2004.
33. "Nanofabrication of Novel Structures for Optical Applications Using Atomic Layer Deposition", Analytical Chemistry Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, October 4, 2004.
34. "Surface Chemistry and Film Growth during  $\text{ZnO}$  Atomic Layer Deposition", *Topical Conference on Science of Semiconductor White Light*, 51st International AVS Symposium, Anaheim, California, November 17, 2004.
35. "Atomic Layer Deposition of Thin Films for Thermal, Optical and Diffusion Barrier Applications", 2004 Discovery Chemistry Seminar, DuPont Central Research and Development, Wilmington, Delaware, December 15, 2004.
36. "Fabrication and Properties of Thin Films Grown Using Atomic Layer Deposition Techniques", Colorado American Chemical Society (ACS) Section Award Talk, ACS Section Meeting, Aspen Room, CU Memorial Center, January 18, 2005.
37. "Atomic Layer Deposition of Metals", Dept. of Chemistry, University of Helsinki, Helsinki, Finland, April 8, 2005.
38. "Atomic Layer Deposition on Polymers", S.M. George, 48th Annual Society of Vacuum Coaters Technical Conference and Smart Materials Symposium, Denver, Colorado, April 27, 2005.
39. " $\text{SiO}_2$  Thin Films Grown Using Atomic Layer Deposition Techniques", 38th Silicon Symposium, University of Colorado, Boulder, Colorado, June 2, 2005.
40. "Scaleup of Atomic Layer Deposition for Coating Large Quantities of Particles", Ferro Electronic Material Systems, Penn Yan, New York, June 16, 2005.
41. "Atomic Layer Deposition on Polymers", Fifteen European Conference on Chemical Vapor Deposition (EUROCVI-15), Bochum, Germany, September 5, 2005.
42. "Atomic Layer Deposition on Polymers", Analytical Chemistry Division Seminar, Department of Chemistry and Biochemistry, University of Colorado, September 19, 2005.
43. " $\text{Al}_2\text{O}_3$  ALD as a Model ALD System", Division of Materials Science and Engineering, Hanyang University, Seoul, Korea, October 4, 2005.
44. "Atomic Layer Deposition on Polymers", SKC Co., Ltd., Seoul, Korea, October 4, 2005.

45. "Atomic Layer Deposition on Polymers", Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea, October 5, 2005.
46. "SiO<sub>2</sub> Thin Films Grown Using ALD Techniques", ASM-Genitech, Daejeon, Korea, October 5, 2005.
47. "SiO<sub>2</sub> Thin Films Grown Using ALD Techniques", Samsung Electronics Co., Ltd., Yongin-City, Gyeonggi-Do, Korea, October 6, 2005.
48. "Enhanced ALD Using Radicals and Catalysts", 2005 Tera Level Nanodevices (TND), Ministry of Science and Technology (MOST), Korean Science and Technology Center, Seoul, Korea, October 7, 2005.
49. "Atomic Layer Deposition on Polymers", College of Natural Sciences, Kookmin University, Seoul, Korea, October 8, 2005.
50. "ALD of W/Al<sub>2</sub>O<sub>3</sub> Nanolaminates: Applications and Challenges", 208th Meeting of the Electrochemistry Society (ECS), Symposium on ALD Applications: Challenges and Opportunities, Westin Bonaventure, Los Angeles, California, October 18, 2005.

## **VII. New Discoveries, Inventions or Patent Disclosures**

The University of Colorado has received and applied for a variety of patents based on the research in Prof. Steven George's research group that has been supported by AFOSR. Previous awarded patents based on AFOSR support include:

1. J.W. Klaus, O.Sneh and S.M. George, "Method of Growing Films on Substrates at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry", U.S. Patent 6,090,442, July 18, 2000.
2. J.W. Klaus and S.M. George, "Method for Forming SiO<sub>2</sub> by Chemical Vapor Deposition at Room Temperature", U.S. Patent Number 6,818,250, November 16, 2004.
3. J.W. Klaus and S.M. George, "A Solid Material Comprising a Thin Metal Film on its Surface and Methods for Producing the Same", U.S. Patent 6,958,174, October 2005.

Patent applications based on AFOSR support currently under review include:

1. S.M. George and C.R. Herrmann, "Al<sub>2</sub>O<sub>3</sub> Atomic Layer Deposition to Enhance the Deposition of Hydrophobic or Hydrophilic Coatings on Microelectromechanical Devices", U.S. Patent Application Number 20050012975.
2. S.J. Henderson and S.M. George, "High Reflectivity and Ultra-High Flux X-ray Optical Element Based on a Graded Multilayer Inside a Monocapillary Tube Fabricated Using Atomic Layer Deposition Techniques", U.S. Patent Application, filed PCT.

3. J.W. Elam, S.M. George, N. Hoivik and Y.C. Lee, "Atomic Layer Deposition of Conformal Protective Coating Layers for Released Microelectromechanical Devices", U.S. Patent Application.

### VIII. Honors/Awards

Over the last three years, Prof. Steven M. George received a number of honors and awards. These were: the University of Colorado Boulder Faculty Assembly Award for Excellence in Research, Scholarly and Creative Work (2006), the American Chemical Society Colorado Section Award (2004), the R&D 100 Award for *Particle-ALD*<sup>TM</sup> (2004) and the Inventor of the Year, University of Colorado at Boulder (2004). Prof. George also has received a National Science Foundation Creativity Award, 2002-2004.

Prof. George has also been elected a Fellow in the American Vacuum Society (2000) and a Fellow in the American Physical Society (1997). Prof. George has also received the Presidential Young Investigator Award (1988-1993) and the Alfred P. Sloan Foundation Award (1988). Prof. George is also very active in the American Vacuum Society (AVS). He was Program Chair for the AVS International Symposium in Boston from Oct. 30-Nov. 4, 2005. He also teaches the AVS one-day short course on Atomic Layer Deposition and has been on the Conference Committee for the *AVS Topical Conference on Atomic Layer Deposition* from 2001-2006.